Application of Nanolimes for the Consolidation of Limestone from the Lincoln Medieval Bishop's Palace

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Abstract
Nanolimes are the first nanomaterials used in heritage conservation for natural stone consolidation. Thanks to their size, they show good penetration depth into the substrates, high reactivity resulting in a faster carbonation process, and the ability to bridge cracks through the formation of a network of calcium carbonate cement.

Two commercial nanolimes (Calosil, IBZ Salztchemie and Nanorestore, CSGI) and a dispersion of $Ca(OH)_2$ nanoparticles, synthesized by an anionic exchange process, were applied to fresh and naturally weathered limestone specimens, previously removed from the Lincoln Medieval Bishop's Palace (Lincoln, UK). A protocol of non-destructive tests was defined to study the treatment effectiveness, both in the laboratory and on-site. The two commercial nanolimes exhibit a low penetration depth, accumulating on the surface and creating a white glazing, and lead to a small increase in surface hardness. On the contrary, the laboratory-synthesized consolidant was able to effect a good superficial consolidation, without affecting the water absorption and aesthetic properties of the specimens. These results, together with those obtained from the application and monitoring of the consolidants on-site, will be crucial for the design of interventive conservation at the Bishop's Palace.

Keywords
Nanolime; consolidation; limestone; built conservation; non-destructive testing

1. INTRODUCTION

One of the main challenges in the conservation of built heritage is the consolidation of natural stone. Different variables need to be considered to identify the degradation mechanisms, to evaluate the state of conservation of the substrates, and to define the conservation actions to carry out, together with the selection of the best materials and methods (Doehne and Price 2010). Calcareous materials have been widely used as building materials, although they are very prone to degradation by weathering mechanisms that can affect their aesthetic, physical and mechanical properties. In particular, the chemical action of atmospheric pollutants such as sulphur and nitrogen oxides (SOx and NOx), and the resulting acid solutions (i.e., acid rain), together with biological activity, freeze-thaw action, and salt crystallisation can compromise the stone mineralogical composition. Moreover, they can create pressure on the pore walls, leading to the weakening of the stone surface (Doehne and Price 2010; Siegesmund and Snethlage 2011).

Consolidants are applied to restore the strength of degraded stone and to reduce further decay (Wheeler 2005). To be used in built conservation, the consolidants must fulfil different requirements. They should improve the stone mechanical properties, by bridging the gaps between grains and cracks. They should show physical and chemical properties compatible with the treated substrate, good adhesion, and penetration depth inside the pores. They should not affect the appearance (colour, texture, gloss), develop harmful by-products, or lead to a complete pore filling, resulting in the reduction of the moisture transfer. Finally, the ideal consolidant should be durable and allow the retreatability of the stone. Silane-based products are the main class of stone consolidants, and among them tetraethyl orthosilicate (TEOS) is the most used on both silicatic and carbonatic stones, as it displays good penetration depth, chemical stability and it does not significantly affect the water vapour properties (Doehne and Price 2010; Wheeler 2005). However, alkoxysilanes poorly bond to calcite grains, and they need long curing time to form the silica gel inside the pores, which is often characterized by cracks developed during the drying process (Doehne and Price 2010; Maravelaki-Kalaitzaki et al. 2006; Sassoni et al. 2016; Wheeler 2005). Acrylic polymers have been employed as consolidants of limestones due to their excellent adhesive properties; however, they display poor penetration and short durability, leading to the formation of cracks in the substrates, due to the physical and mechanical incompatibility with the stone matrix (Charola et al. 1986). Lime-based consolidants have been widely applied for the consolidation of calcareous lithotypes. Limewater is a saturated solution of lime (calcium hydroxide) in water, which has been used to consolidate limestones and plasters for centuries. Limewater is compatible with calcareous stones as calcium carbonate precipitate in the pores of the treated substrates after the reaction of calcium hydroxide with the atmospheric carbon dioxide. Despite the chemical compatibility, limewater is not very effective in the consolidation of weathered stones due to the low concentration of lime particles delivered to the substrate (1.5 g/L). In some cases, due to the micrometric size of the particles, limewater shows a limited penetration in the stone pores, and it usually develops white glazing on the surface. To improve the consolidation effectiveness of lime-based products, in the 1990s nanolime was synthesized and applied in heritage conservation (Salvadori and Dei 2001). It consists of alcoholic dispersion of calcium hydroxide ($Ca(OH)_2$) nanocrystals, in concentrations of 10-50 g/L, with sizes between 50-600 nm (Tzavellos et al. 2019). Thanks to their nanosize and their higher specific surface area, nanolimes are more reactive, resulting in a beneficial reduction of the carbonation time. Compared to limewater, they exhibit better colloidal stability and good penetration into the pores, reducing the formation of a significant white surface layer (C. Rodriguez-Navarro and Ruiz-Agudo 2018). By selecting the most appropriate synthesis route, it is possible to control the particle size, and modulate their chemical reactivity and their properties (Chelazzi et al. 2013). Especially since the introduction of the first commercial products, nanolimes have been widely used for the consolidation of limestones (Giovanni Borsoi et al. 2017; Chelazzi et al. 2013; Daniele et al. 2018; Shekofteh et al. 2019; Giuliana Taglieri et al. 2018; Tzavellos et al. 2019; Zornoza-Indart et al. 2016), lime mortars (Giovanni Borsoi et al. 2017; Delgado Rodrigues et al. 2018; Otero et al. 2018; G. Taglieri et al. 2019) and wall paintings (Chelazzi et al. 2013; Natali et al. 2014). Different factors affect the effectiveness of nanolimes: the concentration of applied suspension and application procedure; the type of solvent and environmental conditions during curing of the treated surfaces, especially in terms of relative humidity and temperature (Chelazzi et al. 2013; Otero et al. 2018). The current research in stone consolidation is focusing on the optimization of the application methodologies of nanolimes on fresh or artificially aged stone specimens, and their effectiveness has been evaluated in laboratory conditions. Only few studies comprise testing of the consolidants on naturally weathered stones to evaluate the interaction of the treatment with lithotypes, characterized by features developed upon ageing and that can not be simulated with artificial procedure (Otero et al. 2019; Tzavellos et al. 2019). In addition, laboratory tests cannot fully reproduce the complexity of outdoor environmental conditions, and only few data on the durability of nanolime treatments applied on-site on naturally aged surfaces are available (Gherardi et al. 2017; Otero et al. 2019; Tzavellos et al. 2019).

The aim of this research is to compare the effectiveness of three nanolime products on sound specimens of a low porosity limestone (Lincolnshire limestone) and naturally weathered limestone specimens, previously removed from the Lincoln Medieval Bishop's Palace (Lincoln, UK). This work allows to set-up the non-destructive testing protocol for the evaluation of the consolidation performance of the products in laboratory, and its optimization for the use on-site. English Heritage is currently carrying out an extended conservation work at the Medieval Bishop's Palace. The results of this study, together with those that will be collected from the application of the consolidants and the 3-years monitoring of their effectiveness on-site, will be crucial for the design of the interventive conservation of the palace.

2. MATERIALS AND METHODS

2.1 Consolidants and their characterization

In this work, three nanolime-based products were tested:

1. CaLoSiL® grey (IBZ-Salzchemie GmbH & Co.KR, Germany): $Ca(OH)_2$ nanoparticles dispersed in ethanol, in a concentration between 5 and 50 g/L, with size of about 50-150 nm. This dispersion is labelled as Calosil.

2. Nanorestore Plus® Propanol 5 (CSGI, University of Florence, Italy): $Ca(OH)_2$ nanoparticles dispersed in 2-propanol, in a concentration of 5 g/L, with size of about 100-300 nm. This dispersion is labelled as Nanorestore.

3. Nanolime dispersion (labelled as LabNanolime) synthesised by an anionic exchange process, according to the procedure developed by Taglieri *et al.* (G. Taglieri et al. 2017): $Ca(OH)_2$ nanoparticles dispersed in 50 - 50% vol. water - 2-propanol, in a concentration of 5 g/L, with size of about 20-80 nm. In particular, the synthesis was carried out by mixing under stirring an aqueous calcium chloride solution with an anion exchange resin (Dowex Monosphere 550A OH, Dow Chemical, USA), at room temperature and ambient pressure, following the previously published synthesis (Otero et al. 2018; G. Taglieri et al. 2016; G. Taglieri et al. 2017; Volpe et al. 2016). $Ca(OH)_2$ nanoparticles are formed by substituting OH groups in the resin with chloride ions (Cl^-) in solution, under conditions of supersaturation, according to the reaction:

$$CaCl_2 + 2(R-OH) \rightarrow Ca(OH)_2\downarrow + 2\,(R-Cl)$$

The concentration of chloride was monitored during the reaction (X30 water strips chloride check, Thermo Fischer Scientific, USA), and the stirring was stopped once the concentration reached constant values below 30 mg/L. The suspension was separated from the resin by using a sieve (100 µm), then the supernatant water was removed and replaced with 2-propanol, to achieve 5g/L concentration in a 50–50% vol. water - 2-propanol dispersion.

In order to study the carbonation process, few drops of each consolidant were applied by pipette as thin film on silicon polished windows (Crystran Ltd, United Kingdom) and stored in a climatic chamber at 25 °C and 65% RH. Fourier Transform Infrared (FTIR) spectroscopy studies were performed on silicon windows coated with the consolidants (64 scans, resolution 4 cm^{-1}) after drying (30 min) and after 7, 15 and 30 days of curing, using a PerkinElmer Spectrum 100 FTIR Spectrometer equipped with a DTGS detector. The background spectra were recorded with silicon windows and subtracted from the sample spectra.

The effectiveness of the nanolime-based consolidants was compared to a tetraethyl orthosilicate (>99%, Sigma Aldrich, Germany), referred to as TEOS.

2.2 Lincolnshire limestone specimens and application of the consolidants

The consolidants were applied on both sound and naturally weathered Lincolnshire limestone specimens. This lithotype is a coarse-grained, creamy white to yellow-orange, ooidal and bioclastic limestone, characterized by porosity values of 13-22%, with average pore sizes of about 1–2 µm in diameter, and pore throats of about 0.1–0.3 µm (Allen et al. 1997; Bottrell et al. 2000; Graham and Stephen 2017). Thanks to its quality and abundance, the limestone has been used and exported as building material since Roman times and it is frequently found in modern and historical architectural structures as the cathedral of Lincoln, the castle and the Medieval Bishop's Palace (Figure 1) (Graham and Stephen 2017).

Before the application of the consolidants, 70 x 10 x 20 mm fresh limestone specimens were washed in deionized water, dried in an oven at 80 °C for 72 hours, and then stored in a climatic chamber at 23 °C and at relative humidity 55%. The consolidants were agitated, and applied by brush until saturation on the top surface by using about 10 mg/cm^2 of consolidant, allowing its complete absorption before the next application (about 1 minute). The specimens were then sponged with a cloth to remove the excess of product. The treated specimens were stored in a climatic chamber at 25 °C and 65% RH for five weeks, then the amount of deposited consolidant in terms of mg/cm^2, denoted as dry matter, was calculated (Table 2). The same procedure was followed for the application of the consolidants on naturally weathered specimens collected from the Medieval Bishop's Palace. To remove contaminants, biofilm and decohesive material, the specimens were cleaned using warm water and a stiff brush. The specimens have irregular shape and different areas (about 100-180 cm^2), and the consolidants were applied on surface exposed to weathering, according to the procedure previously described.

2.3 Evaluation of the treatment effectiveness

The morphology of the specimens before and after the application of the consolidants was studied by strereomicroscopy (Zeiss Stereo Discovery.V8 stereomicroscope) and by Environmental Scanning Electron Microscopy (ESEM) (Inspect S; FEI Inc.) and Energy Dispersive X-ray (EDX) detector (Inca X-ray spectrometer; Oxford Instruments Ltd.). The samples were mounted on aluminium stubs and the ESEM operated at an acceleration voltage of 15 kV.

The evaluation of the surface colour compatibility of the treatments with the stone was carried out by colour measurements, with a Konica Minolta CR-410 Chroma Meter instrument with a D65 illuminant. Measurements were elaborated according to the CIE L*a*b* standard colour system. About 70 measurements were performed on each specimen (3 specimens per treatment) and the average results of L*a*b* were used to calculate the colour difference ΔE between treated and untreated areas: $\Delta E = [(L^*_2-L^*_1)^2+(a^*_2-a^*_1)^2 + (b^*_2-b^*_1)^2]^{1/2})$.

Non-invasive water absorption measurements by contact sponge method were performed using a kit (CTS srl, Italy). The measurements were carried out according to the standard protocol (UNI_11432:2011 2011) (3 specimens per treatment): the sponge was soaked with a 5 ml deionized water syringe and put in contact with the stone surface for 1 min. The sponge mass variation was measured and the water absorption calculated (Wa, g/m^2s).

Finally, the consolidation effectiveness was assessed by non-destructive surface hardness test, using the dynamic rebound testing method according to Leeb, with a rebound device (Proceq Equotip Piccolo 2, Swiss) and single impact method procedure (Desarnaud et al. 2019; Wilhelm et al. 2016). About 50 measurements per specimen (3 specimens per treatment) were collected and the software of the instrument provided the hardness values (HL) expressed in Leeb Hardness unit, which is calculated from the ratio of the rebound velocity (Vr) and impact velocity (Vi), according to (Leeb 1978): HL = Vr/Vi*1000. The surface hardness test was selected to evaluate the impact of conservation treatments on stone specimens, as it is a non-destructive technique, which can be used both in the laboratory and on-site.

3. RESULTS AND DISCUSSION

3.1 Characterization of the consolidants

To study the chemical changes upon drying of the consolidants, FTIR spectra were collected at different times (Figure 2). The spectra obtained from Calosil and Nanorestore after 30 min from the application on silicon windows show a strong and sharp absorption peak at about 3650 cm^{-1} (OH stretching), and a small band at about 1650 cm^{-1} (OH bending), which are distinctive of portlandite (Carlos Rodriguez-Navarro et al. 2013; Carlos Rodriguez-Navarro et al. 2016). With time, the broad band centred at about 1480-1420 cm^{-1} and the band at about 875 cm^{-1}, related to υ_3 asymmetric stretching and υ_2 symmetric deformation of CO_3 groups, respectively, increase and sharpen significantly. In addition, in the spectra collected after 7 days, the broad bands at about 1090 and 1015 cm^{-1} indicate the presence of vaterite and/or aragonite, in addition to calcite (Zhou et al. 2004). On the contrary, the spectra of LabNanolime clearly exhibit the typical peaks of calcite, even after only 30 min since the application, demonstrating a faster carbonation rate of this nanolime. The complete hydrolysis of TEOS was proved by the change of several bands with time (Figure 2d). Peaks at about 2980 (CH stretching), 1170 and 970 cm^{-1} (CH rocking in CH_3) almost completely disappear during curing. In addition, the sharp bands at 1085 (Si-O-C symmetric stretching) and 800 cm^{-1} (ring structure of tetrahedron SiO_4) in the spectrum collected after 30 min broaden and decrease with time, due to the formation of the silica gel (antisymmetric and symmetric stretching Si-O-Si) (Kapridaki and Maravelaki-Kalaitzaki 2013).

3.2 Efficiency of the applied consolidants

Both untreated and treated stone specimens were observed by stereomicroscopy and ESEM-EDX to study the morphology and the distribution of the consolidants (Figure 3 and Figure 4). Optical microscopy images indicate that Calosil and Nanorestore accumulate on the surface, creating a white glazing, clearly visible on fresh specimens, while LabNanolime and TEOS penetrate in the pores, and do not affect the stone morphology (Figure 3 and Figure 4). Additionally, ESEM images also prove a clear reduction of the porosity in stone treated with the two commercial nanolimes, and some cracks can also be observed in the surface layer, probably developed during curing of both products. The accumulation of the product on the surface is not beneficial, as it can obstruct their further penetration in the substrate, reducing the consolidation effectiveness (Giovanni Borsoi et al. 2016). In both fresh and naturally weathered specimens, LabNanolime and TEOS distribute homogenously on the crystals and fill the stone pores, with no changes in the morphology. Previous results indicate that Nanorestore and Calosil tend to form aggregates with size ranging from 200 nm up to 2 µm and from few nanometers to more than 10 µm, respectively (Giovanni; Borsoi et al. 2015; Carlos Rodriguez-Navarro et al. 2013). Being the Lincolnshire limestone characterized by an average pore size diameter of 1-2 µm and with pore throats size ranging 0.1-0.3 µm, the formation of clusters probably compromised the penetration of the commercial nanolimes in the smallest pores, resulting in their accumulation on the surface. On the contrary, LabNanolime tend to form clusters of about 200 nm (G. Taglieri et al. 2017), thus, being able to fill also the smallest pores.

An important requirement of conservation treatment for heritage conservation is the negligible change in the aesthetic properties that they can induce. After the application of Calosil and Nanorestore, a significant increase of the color difference (ΔE) was observed, especially on naturally aged specimens (ΔE values of about 15 and 7 for Calosil and Nanorestrore, respectively), mainly due to the increase of L* and decrease of b*, due to the formation of white glazing (Table 1). This result is in agreement with the microscopic observations, which highlighted the accumulation of the consolidants on the surface. LabNanolime and TEOS do not significantly affect the color of the specimens, due to their good distribution and penetration in the pores (ΔE values lower than 2 and 5.55 on fresh and weathered specimens) (Table 1).

The eventual changes in the water absorption properties of the product after the application of the consolidants were monitored by contact sponge water absorption test. The results obtained on treated fresh and weathered specimens are in agreement with the previous results (ESEM and colorimetry) (Table 2). In particular, Calosil and Nanorestore decrease the water absorption (Wa) (about 60% and 30% for fresh specimens treated with Calosil and Nanorestore, respectively), probably due to the partial filling of the pores by the consolidant in the stones surface and a change in the pore size distribution (Gherardi et al. 2018). Specimens treated with LabNanolime and TEOS exhibit irrelevant reduction of Wa (Table 2), proving the effective coverage of the pores, without leading to complete pore filling.

The consolidation effectiveness of the treatments was evaluated by surface hardness test. Surface hardness tests are non-destructive and have been used to characterize the stone decay (Wilhelm et al. 2016) and to assess the impact of consolidants applied on stone (Wedekind et al. 2016; Zornoza-Indart et al. 2016; Zornoza-Indart and Lopez-Arce 2016) and wall paintings (Pondelak et al. 2017). Untreated fresh specimens show slightly higher hardness values (HL) compared to the naturally weathered ones (Table 2), due to the higher cohesion of the minerals on the surface. After the application of the consolidants, an increase in HL values was observed in every specimen, as a result of the increase of surface cohesion (Zornoza-Indart and Lopez-Arce 2016), and similar ΔHL values were obtained for fresh and aged specimens treated with Calosil, Nanorestore and TEOS (ΔHL values of about 10%, 8% and 8% for Calosil, Nanorestore and TEOS, respectively). The surface hardness of a stone is associated to its mineralogical composition and cohesion; therefore, an increase of hardness suggests higher cohesion of the substrate (Zornoza-Indart et al. 2016). A higher increase in the HL values was obtained in naturally aged specimens treated with LabNanolime, with ΔHL of about 20%, compared to fresh specimens (ΔHL of about 12%) (Table 2). This is probably due to the difference in the pore size distribution of fresh and weathered limestone, and the latter promoting a higher absorption of the consolidant in the pores, a better penetration and bridging of cracks grains with well-shaped calcite cement (Otero et al. 2018), with a consequent increase in the consolidation effectiveness.

4. CONCLUSIONS

In this work, the effectiveness of three nanolime-based consolidants and TEOS applied on fresh Lincolnshire limestone and naturally weathered specimens collected from Lincoln Medieval Bishop's Palace was evaluated, following a protocol of non-destructive tests. The results obtained from fresh and weathered specimens are comparable; they prove that the consolidants show different effectiveness, and that they increase the stone surface hardness, especially after the treatment with the laboratory synthesized nanolime (LabNanolime). Calosil and Nanorestore were shown to fill the pores of the stone, inducing a reduction in the water absorption, and to accumulate on the surface, creating white glazing. LabNanolime does not lead to significant changes in the water absorption nor the aesthetic properties of the stone, and exhibits the highest surface hardness increase, as a result of the increase of surface cohesion after consoldiation.

The same consolidants will be applied on-site, in different areas of the Medieval Bishop's Palace and the same non-destructive testing protocol will be carried out, to evaluate the treatment efficacy on surfaces exposed to different environmental parameters and to monitor them over time (3 years). The results will be relevant for the design of the conservation works on the surfaces of the historic building.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Figure 1. Images of the Medieval Bishop’s Palace in Lincoln and of the Lincolnshire limestone blocks.

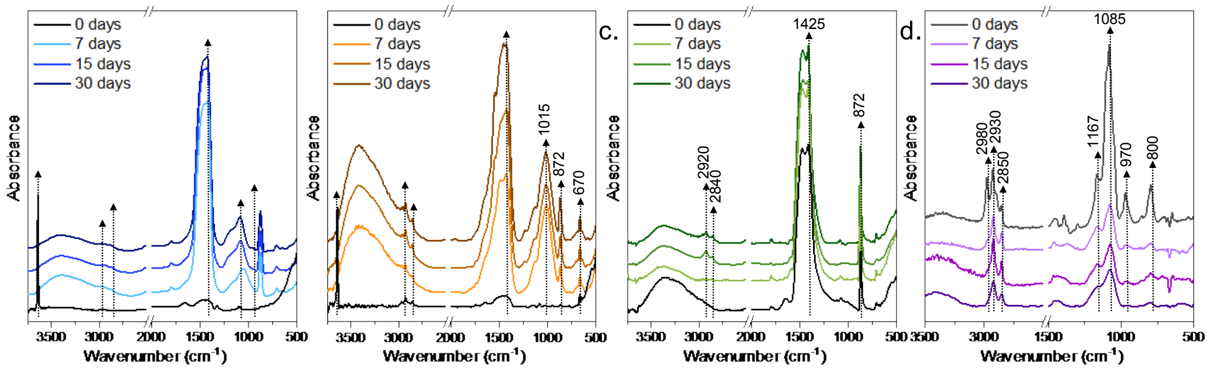

Figure 2. Fourier-Transform Infrared (FTIR) spectra of Calosil (a.), Nanorestore (b.), LabNanolime (c.) and TEOS (d.) collected at different times.

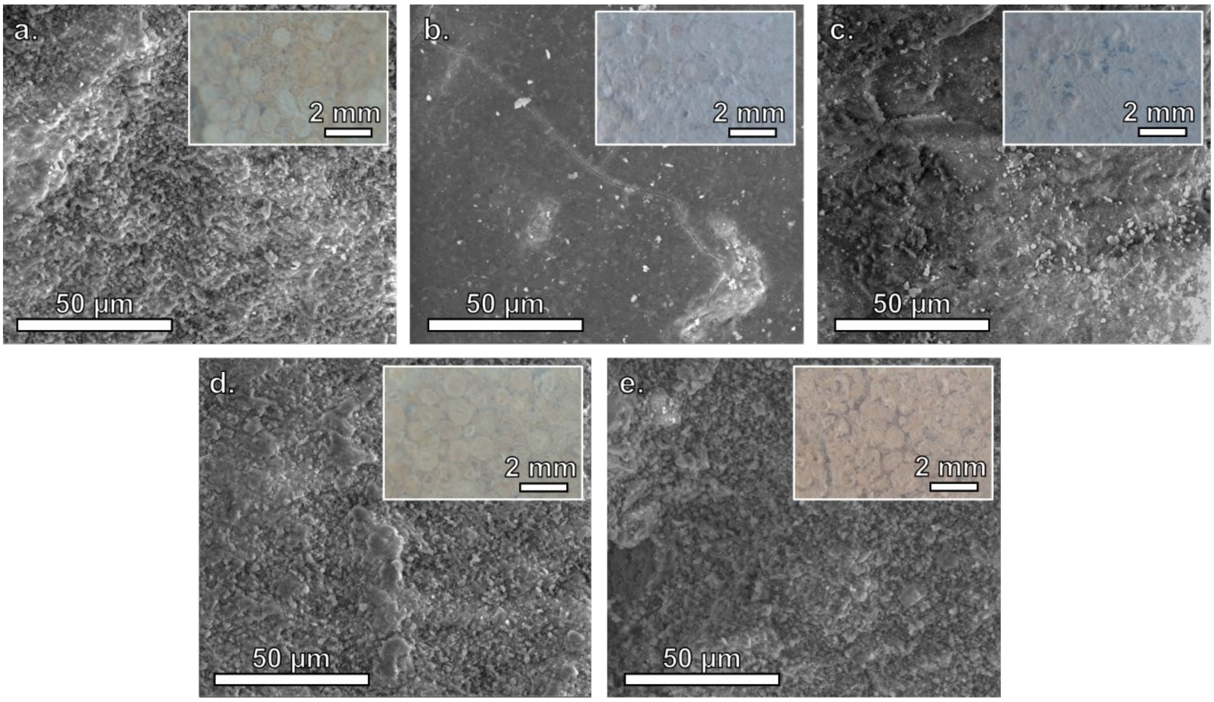

Figure 3. Optical and Environmental Scanning Electron Microscope (ESEM) images of fresh limestone specimens before (a.) and after the application of Calosil (b.), Nanorestore (c.), Lab Nanolime (d.) and TEOS (e.).

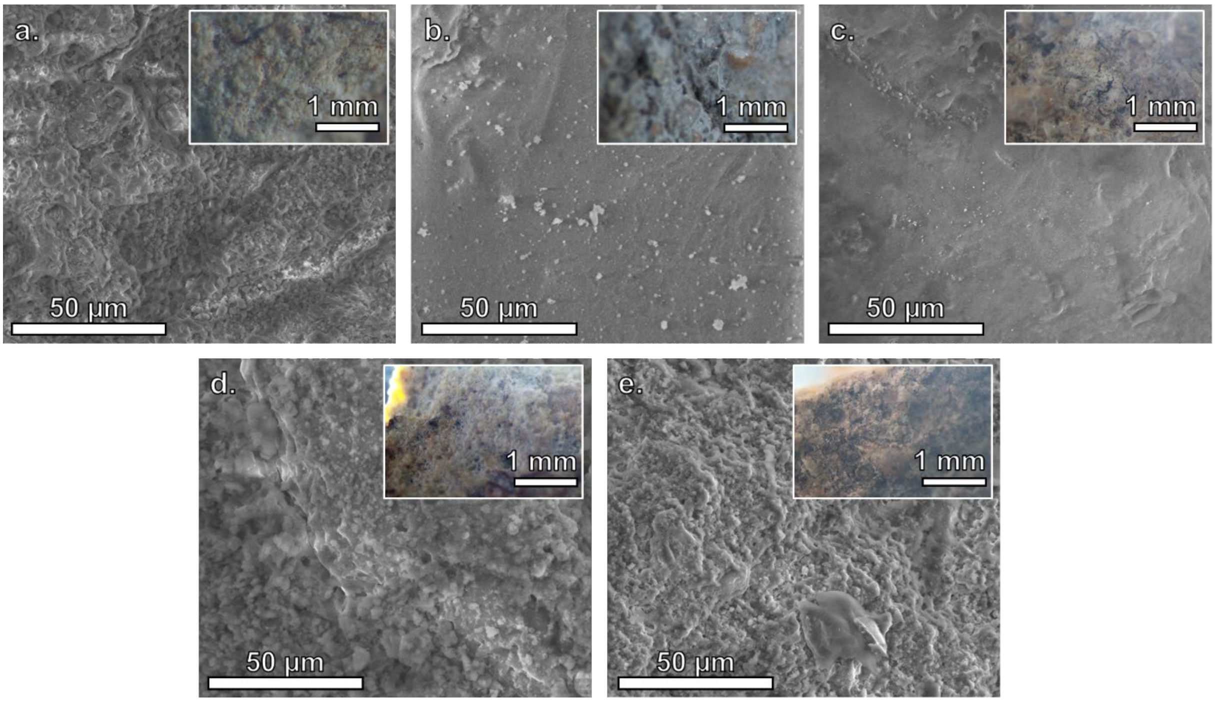

Figure 4. Optical and Environmental Scanning Electron Microscope (ESEM) images of specimens collected from the Medieval Bishop's Palace before (a.) and after the application of Calosil (b.), Nanorestore (c.), Lab Nanolime (d.) and TEOS (e.).

Table 1. ΔE, ΔL*, Δa* and Δb* data obtained from colorimetric measurements on fresh limestone specimens and specimens collected from the Medieval Bishop's Palace before and after the application of the consolidants.

Specimens	Consolidant	ΔE	ΔL*	Δa*	Δb*
Fresh limestone	Calosil	8.19±0.82	1.10±0.45	0.48±0.07	-8.10±0.79
	Nanorestore	5.23±0.20	1.34±0.42	0.25±0.11	-5.04±0.16
	LabNanolime	1.46±0.26	-1.08±0.20	0.53±0.04	0.83±0.24
	TEOS	0.19±0.15	0.09±0.03	0.04±0.02	0.09±0.22
Specimens from Medieval Bishop's Palace	Calosil	15.08±0.75	5.49±0.54	-1.04±0.13	-14.01±0.61
	Nanorestore	6.83±1.60	4.89±3.87	0.35±1.00	-3.65±2.28
	LabNanolime	5.55±0.30	3.40±0.78	0.60±0.23	-4.30±1.01
	TEOS	1.93±1.21	1.07±0.01	0.42±0.50	-1.32±1.61

Table 2. Values of average dry matter (mg/cm^2) of consolidants applied by brush on stone specimens. Water absorption ratios (Wa) and surface microhardness (HL units) measured on fresh limestone specimens and specimens collected from Medieval Bishop's Palace before and after the application of the consolidants (surface after treatment: Wa_t and HLD_t; surface before treatment: Wa_{nt} and HLD_{nt}).

Specimens	Consolidant	Dry matter (mg/cm^2)	Wa_t/Wa_{nt}	HL_{nt}*	HL_t	ΔHL (%)
Fresh limestone	Calosil	2.4±0.4	0.43±0.07	397±37	436±33	10
	Nanorestore	2.4±0.3	0.70±0.07	425±49	457±49	8
	LabNanolime	2.3±0.3	0.81±0.01	467±11	522±13	12
	TEOS	4.0±0.4	0.93±0.01	377±2	406±4	8
Specimens from Medieval Bishop's Palace	Calosil	4.2±0.3	0.66±0.08	349±25	384±26	10
	Nanorestore	3.5±0.4	0.72±0.04	364±38	392±29	8
	LabNanolime	4.1±0.3	0.99±0.35	307±1	365±13	19
	TEOS	5.1±0.4	1.00±0.22	365±8	393±16	8